

ASYMMETRIC OXIDE-CERAMIC MEMBRANES BASED ON ALUMINOSILICATES

T. P. Salikhov,¹ V. V. Kan,¹ É. M. Urazaeva,¹ T. V. Savatyugina,¹ G. M. Arushanov,¹
and S. N. Kan^{1, 2}

Translated from *Steklo i Keramika*, No. 8, pp. 22–27, August, 2014.

The precipitation of a heterogeneous polydisperse suspension of low hydrophylicity onto an aluminosilicate substrate is used to obtain ceramic membranes with an asymmetric structure. The average pore size of the ceramic membrane is 0.3–0.5 μm . The problem of matching the shrinkage of the ceramic substrate and membrane layers is solved. A technology for obtaining micro- and ultrafiltration membranes using suspensions based on water and alcohol-water solutions of carboxymethyl cellulose is presented.

Key words: membranes, ceramic, asymmetric structure, permeability, pore size, hydrophylicity, suspension, substrate, shrinkage, layers, water solution.

An analysis of the literature shows that ceramic single-layer membranes are unpromising because of their instability and low permeability. The appearance of asymmetric membranes became a breakthrough in their industrial application. Such construction makes it possible to combine membrane selectivity with a high rate of mass transfer [1].

The ceramic materials of membranes comprise compounds of metal with nonmetals in the form of oxides, nitrides, phosphates, and carbides. Oxide ceramic membranes are most common and available on an industrial scale. Some of the main natural resources for the production of oxide ceramic are kaolin clays owing to their wide occurrence and relatively low cost. Ceramic materials with different characteristics, such as shrinkage, strength, porosity and so forth, can be obtained from one and the same kaolin clay.

Thin selective layers on a substrate cannot be obtained without taking account of sintering processes associated with shrinkage phenomena in a ceramic membrane article. However, the mismatch between the shrinkages of the selective layers and the substrate can be substantial, and this is one of their problems. The technology of obtaining multilayer ceramic membranes must take account of the compatibility of the materials during high-temperature firing of articles [2]. In addition, a difficulty in implementing the ceramic techno-

logy is that many parameters influence the final properties of the membrane article. Hence follows the still relevant problem of optimizing the composition of the ceramic batch.

All methods of conventional ceramic technology are used to form the porous carrying substrates of ceramic membranes: pressing, extrusion, slip and centrifugal casting [3]. And sol-gel [4] and suspension methods are used to form micro- and ultrafiltration selective layers on a porous substrate.

Analysis of the scientific and technical literature and patents on the technology of obtaining asymmetric ceramic membranes has shown that the main part of the work using suspensions is directed toward solving two problems [5–7]:

- obtaining and preserving the uniformity of the distribution of the components during sedimentation deposition of a polydisperse suspension on a substrate;
- preventing the layers from merging with one another and formation of a boundary with the highest possible contrast between the substrate and the membrane layer.

In the overwhelming majority of the technologies used to obtain ceramic membranes it is expected that polydisperse compositions containing sintering and plasticizing additives differing sharply with respect to size and morphology from the main component will be used.

To reduce the effect of deep penetration of a suspension into the pores of the substrate, which results in the appearance of microcracks and microchannels, a technology for reducing the hydrophylicity of the substrate or the suspension itself is used.

¹ Institute of Materials Science, Scientific-Industrial Association 'Solar Physics', Academy of Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan.

² E-mail: valery-kan1957@yandex.ru.

TABLE 1. Effect of Preliminary Heat-Treatment of Fireclay on the Sintering of the Filtering Ceramic (Sintering Temperature of the Pressed Substrates 1190°C)

Batch content, %	Preliminary firing temperature of the fireclay, °C	Substrate shrinkage, %	Filtering properties	
			d_{\max}/d_{av} , μm	K , μm^2
Fireclay – 80;	1400	4.47	16.2/9.9	0.60
bentonite – 15;	1300	6.94	13.2/7.8	0.28
glass – 5	1250	7.70	7.4/3.7	0.10
	1200	9.70*	–	–

* Deformation of the sample.

The technologies used for the production of polymer membranes are now well developed and widely used [1], in contrast to the technologies used to form ceramic membranes, which are still being actively developed. The technological investigations performed in earlier research [8, 9] on the development of multilayer filtering structures with strong adhesion of the layers and narrow pore-size distribution formed the basis for taking account of the specific features of the technology for producing membrane structures.

In this article we present research on the influence of a wide spectrum of technological techniques for obtaining a uniform thin layer of a membrane coating based on heterogeneous aluminosilicates materials.

The process of fabricating ceramic membranes consists of the following stages:

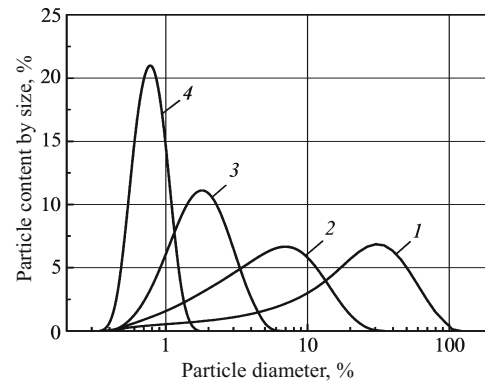
- obtaining ultrafine fractionated powders;
- obtaining a macroporous substrate;
- preparing a paste for deposition on a substrate;
- depositing a selective layer;
- drying and high-temperature firing of the composition obtained.

The following were used as the initial materials for the production of porous ceramic: fireclay (filler with different fractions), kaolin and bentonite clays (binder), cullet (sintering additive), and a water solution of carboxymethyl cellulose CMC (plasticizing additive).

An important factor influencing the formation of a porous structure of the forthcoming permeable ceramic is the fractional composition of the powders.

To obtain fractionated powders for producing the structural framework of the filtering material, the initial kaolin was fired at 1200 – 1400°C and subjected to crushing, grinding in a ball mill, and sedimentation [10]. The fractional composition of the initial materials was investigated with the aid of a Malvern laser particle-size analyzer.

The investigation and determination of the structural particularities of the ceramic membranes were performed mainly by means of gas-liquid porometry [11, 12]. The method gives an idea of the permeable pores of the selective layer, in contrast to the method of mercury porometry, which

**Fig. 1.** Particle-size distribution of the ceramic powders of fireclay: 1) fraction for obtaining the carrying porous substrate; 2, 3) fractions for obtaining intermediate layers; 4) fraction for membrane layers.

measures the total value of the permeable and blind pores of the entire membrane together with the substrate.

Gas-liquid porometry makes it possible to determine clearly and with a high degree of accuracy not only the maximum size of the pores, but also the size distribution of the filtering pores and the degree of defectiveness of the membrane obtained.

Ceramics for Substrates. Flat microporous substrates were prepared by uniaxial pressing of a ceramic batch under pressure 5 – 10 MPa. The pressed samples were fired in air in electric furnaces at 900 – 1190°C.

The effect of the preliminary firing of the fireclay on the characteristics of the substrates obtained for the membranes was investigated. Samples with the following compositions were obtained on the basis of fireclay with different degrees of firing (1200, 1250, 1300, 1400°C) and investigated (content by weight, %):³ fireclay — 80, bentonite (kaolin) — 15, and glass — 5. The fractional composition of the fired fireclay after grinding and sieving is presented in Fig. 1. The curve 1 showing the particle distribution in the powder is asymmetric with a maximum at 30 – 35 μm . The shrinkage and filtering properties of the samples (size of the permeable pores d_{\max}/d_{av} , gas permeability K) were investigated.

The shrinkage of the substrate samples increased with decreasing preliminary firing temperature of the fireclay (up to deformation of the samples). The pore sizes and the permeability were minimal when using fireclay fired at 1250°C.

A series of samples in which the percentage content of glass and the nature of the binding clay additive was prepared for a detailed investigation of the shrinkage phenomena in ceramic for substrates with the use of fireclay fired at 1250°C.

It was established that a 1% reduction in the glass content decreases the shrinkage from 7.7 to 5.96% (samples 1 and 3, respectively). The samples with different contents of

³ Here and below, the content by weight, %.

kaolin as the binder and with constant content of the sintering additive at 7% showed a clear tendency toward suppression of the shrinkage processes with increasing kaolin content in the batch.

The experiments on the use of substrates with different degrees of firing showed that substrates pre-fired at 900°C are most practicable for subsequent deposition of membrane layers. Raw (unfired) blanks soften and lose shape, which makes it difficult to obtain a uniform selective layer.

Suspensions for Selective Layers. The process of obtaining fine powders includes heat treatment, prolonged grinding of fireclay, sedimentation of the powder under gravity, and mixing of the components (fireclay, kaolin, glass) in a planetary mill.

The technology for depositing selective layers on a substrate was developed using a suspension composition that corrects the shrinkage between the layers with different fractional composition during sintering (suspension composition, %): fireclay — 80 – 81.5, kaolin — 15, glass — 3.5 – 5.

The reduction of the amount of glass compared with the substrate is due to the tendency of very fine powders to sinter at lower temperatures.

The suspensions were prepared on the basis of sedimentation powders of heat-treated (at 1400°C) fireclay with particle sizes < 20 μm , < 5 μm , < 2 μm (Fig. 1, curves 2, 3, 4). The smaller the fraction, the more symmetric the particle-size distribution curve is. The content range of the solid phase of suspensions varied from 7 to 20%.

Water and water solutions of polymers (CMC) were used to prepare the suspensions. The introduction of a polymer increases the viscosity of the suspension, which makes it possible to reach the necessary thickness of the selective layer, increases the sedimentation stability of the composition and prevents coagulation of the particles. This excludes to a large degree the formation of cracks during drying and firing of membranes. The coating deposition time and the number of layers deposited were varied and recorded.

Intermediate Layers. A technology based on water suspensions was used to deposit the coatings. The content of the solid phase of the suspensions was varied over wide limits and equaled 15% for powder with 20 μm particle size and 13% for 5 μm . These values are optimal, since subsequent increases in the solid-phase content to 20% resulted in a sharp increase in the viscosity of a suspension and thickness of the coating layer (> 1 mm).

Covering of large pores during one-step deposition of the fraction < 5 μm was not observed because particles fell into the pores in the substrate. One-step deposition onto a substrate of a suspension based on powder with particles < 20 μm followed by high-temperature firing made it possible to decrease the minimum pore size from 11 to 1.9 μm . Covering of the largest pores does not occur in the substrate (Table 3, sample 2). Deposition of the second layer with 5 μm powder results in a sharp reduction of the size of all

TABLE 2. Effect of Sintering Additives on the Shrinkage of Filtering Ceramic (Substrate), Fired at Temperatures 1190°C

Substrate sample no.	Content, wt. %				Shrinkage
	Fireclay*	Bentonite	Kaolin	Glass	
1	80	15	—	5	7.70
2	80.5	15	—	4.5	6.20
3	81	15	—	4	5.96
4	78	7.5	7.5	7	6.40
5	78	—	15	7	5.83
6	63	—	30	7	5.45

* Firing temperature 1250°C.

TABLE 3. Pore Size in Intermediate Layers versus the Content by Weight of the Solid Phase in a Water Suspension

Index	Samples					
	1	2	3	4	5	6
Suspension:						
mass fraction of the solid phase, %	0/0	15/0	15/13	7.5/6.5	3.75/6.5	3.75/13
Intermediate layer:						
d_{\min} , μm	11.0	1.9	1.4	6.8	8.3	8.3
d_{\max} , μm	20.1	19.8	1.7	16.0	18.0	17.4
K , μm^2	0.24	0.21	0.17	0.18	0.24	0.19

* Solid phase of the 20 μm fraction (numerator); solid phase of the 5 μm fraction (denominator).

permeable pores (sample 3). However, individual defects of size 9.9 μm are encountered.

Experiments on the dilution of suspensions showed that any reduction of the concentration below the optimal level results in a reduction of the density of the solid phase of the precipitate and increases the size of all permeable pores (samples 4 – 6).

Membrane Coatings Based on Water Solutions of Suspensions. Samples of asymmetric ceramic membranes were obtained by successive three-layer deposition of water suspensions based on fine powders. Blanks fired at temperature 900°C served as substrates. The final firing of the membranes was performed at 1190°C.

Covering of the pores in a ceramic membrane is shown in Fig. 2. The pore size depends on the size of the solid phase of the suspension. Sintering the layers based on large fractions makes it possible to obtain pores which are an order of magnitude smaller than the initial powder. The pore size of the membrane layers decreases 4 – 5-fold. The thickness of the coating is 300 – 500 μm . Defects reach 1 – 3 μm in size.

Analysis showed that the difference in the shrinkage of the substrate and selective layer causes the surface of flat

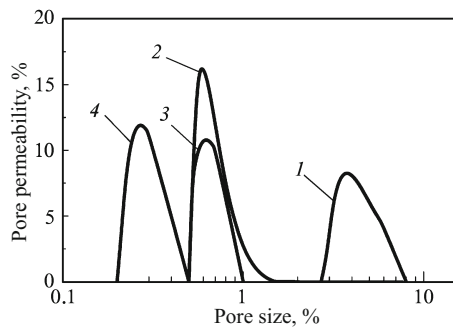


Fig. 2. Size distribution curves of permeable pores in a ceramic three-layer membrane, obtained by successive deposition of the suspension based on water solutions of powders: 1) substrate based on powder $< 100 \mu\text{m}$; 2, 3) intermediate layers based on powder $< 20 \mu\text{m}$ and $< 5 \mu\text{m}$; 4) membrane layer based on powder $< 2 \mu\text{m}$.

samples to curve. A drawback of the technology using water suspensions is the high hydrophilicity of the suspension with respect to the substrate, which imparts to it high absorbency and allows the membrane layers to penetrate into the substrate material. As a result thick layers are formed and the boundary layer between the substrate and the membrane becomes smeared. Wedging phenomena occurring during firing of articles give rise to defects in the form of microcracks. Since a suspension is heterogeneous in terms of particle-size and chemical composition, the layers of the system separate and vitrified sections are formed during mass production of filtering elements based on fireclay.

Obtaining Membrane Coatings by Deposition of Suspensions Containing Solutions of Carboxymethyl Cellulose (CMC). A method was developed to increase the viscosity of a suspension by adding polymers in order to eliminate

the drawbacks of water suspensions. A solution of CMC with a wide range of concentrations was used as a polymer binder. The reduction of the hydrophilicity of the suspension made it possible to deposit membrane layers directly on a substrate without using intermediate layers.

Data on the technology of depositing coatings with size fractions $< 2 \mu\text{m}$ followed by firing of the membrane elements are presented in Table 4.

Suspensions based on 3% CMC solutions deposited on substrates fired at 900°C did not give positive results. The coatings cracked during drying and heat-treatment. Preliminary firing of a substrate at 1190°C made it possible to obtain a coating with satisfactory appearance, but investigation of the filtering properties showed hardly noticeable covering of pores in the substrate. A water solution of a suspension of 0.3% CMC is optimal.

Such a solution made it possible not only to obtain a continuous coating on substrates fired at 900°C but also to cover its pores effectively. The deposition of two layers gave an ultrafiltration membrane with $0.3 - 0.5 \mu\text{m}$ pores. The drawback is the presence of individual micron-size defects.

Obtaining Membrane Coatings Based on Suspensions with Low Hydrophilicity by Introducing Polymer Additives and Ethyl Alcohol. The introduction of a polymer binder based on CMC results in a reduction of hydrophilicity of the suspension, prevents the suspension from penetrating into the interior volume of the substrate, and increases its sedimentation stability, which prevents separation of heterogeneous compositions.

This made it possible to obtain continuous films on the surface of a substrate. However, the increased viscosity makes it possible for numerous air bubbles to appear in the suspension as well as problems with the thickness of the coatings. Alcohol-water solutions with CMC mass fraction from 2 to 5% were used to eliminate these phenomena (Table 5).

Suspensions with the addition of alcohol make it possible to develop thin coatings on substrates of any kind. Membrane layers with average pore size to $0.3 \mu\text{m}$ can be obtained by depositing suspensions of powder with particle size $< 2 \mu\text{m}$. The thickness of the selective layer can vary from 30 to $300 \mu\text{m}$.

Membrane elements based on aluminosilicates ceramic with a composition gradient were obtained. The shrinkage mismatch was eliminated by decreasing the amount of sintering additive in the form of glass in selective layers as well as by using different plasticizing additives in the form of kaolin and bentonite for the selective layers and substrate, respectively.

The processes of deposition of three types of dispersion media for suspensions were investigated: on basis of a water medium, 0.3 – 3% water solutions of the polymer CMC, and 3% alcohol-water solutions of CMC.

Membrane elements with pore size $0.25 - 0.5 \mu\text{m}$ with the presence of individual micron-size microdefects and

TABLE 4. Characteristics of Membrane Elements Obtained by Deposition of Suspensions Based on Water Solutions of CMC

Index	Membrane sample		
	1	2	3
Substrate firing temperature, $^\circ\text{C}$	1190	1190	900
CMC content, wt. %	3	0.3	0.3
Substrate:			
shrinkage, %	4.9	5.7	4.5
$K, \mu\text{m}^2$	0.16	0.12	0.06
$d_{\text{max}}/d_{\text{av}}, \mu\text{m}$	9/5.1	9.4/4.3	8/2.4
1st layer:			
shrinkage, %	4.9	5.75	4.5
$K, \mu\text{m}^2$	0.14	0.12	0.03
$d_{\text{max}}/d_{\text{av}}, \mu\text{m}$	8.8/4.8	9.5	1/0.5
2nd layer:			
shrinkage, %	4.9	—	4.5
$K, \mu\text{m}^2$	0.11	—	0.02
$d_{\text{max}}/d_{\text{av}}, \mu\text{m}$	8.3/4.4	—	0.5/0.3

TABLE 5. Characteristics of Membrane Elements Obtained by Deposition of Suspensions Based on Alcohol-Water Solutions of CMC

Membrane sample	Substrate			Membrane layer		
	Substrate firing temperature, °C	K , μm^2	$d_{\text{max}}/d_{\text{av}}$, μm	Membrane firing temperature, °C	K , μm^2	$d_{\text{max}}/d_{\text{av}}$, μm
1	900	0.06	8/3.1	1000	0.01	0.5/0.3
2	1190	0.03	8.3/2	1000	0.02	0.5/0.3

thickness of membrane layers to 300 μm were obtained by repeated deposition of water solutions of suspensions.

CONCLUSIONS

Thin films on practically all types of substrates were obtained on the basis of 3% alcohol-water solutions of CMC. Asymmetric membranes with average pore size 0.3 μm and thickness 30 – 50 μm were obtained on the basis of suspensions of this type.

It should be noted that the determination of the maximum pores and the entire interval of permeable pores of a membrane element was made by an improved method of gas-liquid porometry.

REFERENCES

1. M. Mulder, *Introduction to Membrane Technology* [Russian translation], Mir, Moscow (1999).
2. V. V. Zyryanov, "Multilayer ceramic membranes with selective permeability," *Konstr. Kompozit. Mater.*, No. 1, 32 – 49 (2007).
3. Yu. I. Komolikhov and L. A. Blagina, "Technology of ceramic micro- and ultrafiltration membranes (review)," *Ogneup. Tekh. Keram.*, No. 5, 20 – 28 (2002).
4. N. G. Medvedkova, and V. V. Nazarov, "Sol-gel process for obtaining selective layers of ceramic ultrafiltration membranes based on titanium oxide," *Steklo Keram.*, No. 4, 20 – 22 (1996); N. G. Medvedkova and V. V. Nazarov, "Sol-gel preparation of selective layers of ceramic ultrafiltration membranes based on titania," *Glass Ceram.*, **53**(4), 117 – 119 (1996).
5. *Composite Ceramic Micropermeable Membrane, Process and Apparatus for Producing Such Membrane*, Patent EP320023, June 14, 1989, IPC B01D39/20; B01D67/00; B01D69/02; B01D69/04; B01D71/02; B05C3/18; B05C7/04; C04B38/00; C04B41/50; C04B41/52; C04B41/87; C04B41/89.
6. *Structure de Filtration, Procédé de Realisation de Telles Structures et Dispositif D'ultrafiltration en Comportant*, Patent FR2502508, October 1, 1982, IPC B01D39/20; B01D61/18; B01D63/06; B01D71/02; B01D71/04; C04B38/00; C04B41/50; C04B41/87.
7. *Membrane Separation Apparatus and Methods for Making the Same*, Patent FR2560526, September 6, 1985, IPC B01D63/00; B01D63/06; B01D71/02.
8. T. P. Salikhov, V. V. Kan, É. M. Urazaeva, et al., "Corundum filtering ceramic with phosphate binders," *Steklo Keram.*, No. 8, 28 – 31 (2008); T. P. Salikhov, V. V. Kan, E. M. Urazaeva, et al., "Kan Corundum filtering ceramic with phosphate binders," *Glass Ceram.*, **65**(7 – 8), 278 – 281 (2008).
9. T. P. Salikhov, V. V. Kan, É. M. Urazaeva, et al., "Formation of selective layers of ceramic membranes based on oxide powders fused in a solar furnace," *Geliotekhnika*, No. 2, 58 – 64 (2007).
10. P. A. Kouzov, *Fundamentals of Analysis of the Particle-Size Composition of Industrial Dust and Comminuted Materials* [in Russian], Khimiya, Leningrad (1987).
11. T. G. Plachenov and S. D. Kolosentsev, *Porometry* [in Russian], Khimiya, Leningrad (1988).
12. Yu. N. Kryuchkov, "Evaluation of the parameters of a porous structure of ceramic filtration materials," *Ogneup. Tekh. Keram.*, No. 11, 15 – 18 (1997).